This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Antimicrobial Properties of Diamondlike Carbon-Silver-Platinum Nanocomposite Thin Films

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Abstract

Silver and platinum were incorporated within diamondlike carbon (DLC) thin films using a multicomponent target pulsed laser deposition process. Transmission electron microscopy of the DLC-silver and DLC-platinum composite films reveals that the metals self-assemble into particulate nanocomposite structures. Nanoindentation testing has shown that diamondlike carbon-silver films exhibit hardness and Young's modulus values of approximately 37 GPa and 333 GPa, respectively. DLC-silver-platinum films exhibited antimicrobial properties against *Staphylococcus* bacteria. Diamondlike carbon-biofunctional metal nanocomposite films have a variety of potential medical and antimicrobial applications.

Keywords: diamondlike carbon, pulsed laser deposition, thin films

Introduction

Biomedical researchers have created advanced materials over the past three decades by selecting bulk materials with appropriate fracture toughness, bulk modulus, and durability, and performing surface modification to improve biocompatibility, wear resistance, and corrosion resistance. One ceramic coating with tremendous potential for medical applications is diamondlike carbon (DLC). The term diamondlike carbon (DLC) describes hydrogen-free hard carbon solids that possess a cross-linked, non-crystalline network of sp^2- and sp^3- hybridized carbon atoms [1]. The friction and wear coefficients of DLC are lower than those of diamond, and are among the lowest recorded to date (static coefficient of friction= 0.006). DLC also offers transparency to light ranging from deep ultraviolet to far infrared. In addition, DLC films are amorphous, atomically smooth, and do not contain open corrosion paths to the underlying substrate.

Diamondlike carbon thin films have also been shown to possess excellent cell compatibility. For example, *in vitro* studies of diamondlike carbon films involving mouse peritoneal macrophages, mouse fibroblasts, human myeloblastic ML-1 cells, osteoblast-like cells, and human embryo kidney 293 cells have demonstrated the absence of an inflammatory response [2-5]. Morphological and biochemical data suggest that DLC-exposed cells undergo no cellular damage. For example, osteoblast-like cells exposed to DLC coatings have not shown any change in the production of alkaline phosphatase, type I collagen, or osteocalcin [6]. In addition, neuronal growth readily occurs on DLC surfaces [7]. Diamondlike carbon thin films have been recently considered for a variety of cardiovascular, orthopaedic, ophthalmic, biosensor, and implantable

microelectromechanical system applications, which allow for improved device lifetimes and unique interactions with the biological environment.

Pulsed laser deposition of diamondlike carbon involves laser ablation of a sp^2 bonded carbon target, which results in the formation of a sp^3- and sp^2- bonded film. The most common target material is high purity graphite; other target materials have included pressed diamond powder, glassy carbon, and polymer [8-10]. Pure carbon sources lead to pure DLC films, whereas hydrocarbon sources lead to DLC films with significant hydrogen and/or hydrocarbon incorporation. The reported growth rates of DLC films deposited using a 248 nm excimer laser are on the order of 0.01 nm/pulse [11]. Laser processing of diamondlike carbon thin films involves several interdependent factors, which include: (1) kinetic energy of the carbon species, (2) background pressure, and (3) substrate temperature. These parameters have tremendous bearing on diamondlike carbon film properties, including the sp^3/sp^2 ratio, the adhesion of the DLC film to the substrate, and the amount of sp^2 clustering [12].

We have recently developed a variant of the conventional pulsed laser deposition process in order to incorporate biofunctional metals during DLC film deposition. Briefly, a single multicomponent target is loaded into the pulsed laser deposition chamber. This target contains pure graphite that is covered by a piece of the desired modifying element (Figure 1). The focused laser beam sequentially ablates the graphite target component and the modifying element target component to form composite layers. The metal composition in these films can be controlled through altering the following parameters: (1) the scanning radius of the laser beam on the target surface, (2) the laser beam position, (3) the position of the circular target, (4) the size of the metal piece on the

target, and (5) the laser energy density. The fraction of metal atoms incorporated into the diamondlike carbon film can be estimated using the following relation:

$$\text{fraction of metal within diamondlike carbon-metal nanocomposite film} = \alpha\,\delta\,(1-R_d)/2\,\pi\,\gamma(1-R_c) \quad [1]$$

in which α is the laser ablation ratio, γ is the laser beam scanning radius, R_c is the reflectivity of carbon, R_d is the reflectivity of the metal strip, and δ is width of the metal piece. We have prepared several diamondlike carbon-metal nanocomposite films using this modified pulsed laser deposition process. These films were examined using transmission electron microscopy, electron energy loss spectroscopy, visible Raman spectroscopy, nanoindentation, and microbial biofilm attachment testing.

Experimental

Several 1 cm x 1 cm pieces of silicon (100) were cleaned in acetone and methanol within an ultrasonic cleaner. The silicon substrates were subsequently dipped in hydrofluoric acid to remove silicon oxide, which resulted in a hydrogen-terminated surface. The Lambda Physik LPX 200 KrF excimer laser (248 nm wavelength) was used for ablation of the multicomponent graphite/metal target. Pieces of silver and platinum were placed over the graphite target, which was rotated at 5 rpm throughout the deposition. The laser was operated at a frequency of 10 Hz and a pulse duration of 25 ns. The laser energy output of 215 mJ and laser spot size of 0.043 cm^2 imparted an average

energy density of ~ 5 J/cm^2 to the target. The target-substrate distance was maintained at 4.5 cm.

High resolution Z-contrast images were obtained using a JEOL 2010 F scanning transmission electron microscope equipped with field emission gun and Gatan Image Filter (GIF). In STEM-Z contrast imaging, large angle scattered electrons are collected with an annular detector. The resulting contrast is proportional to atomic number squared (Z^2). Parallel electron energy loss spectroscopy was used to obtain information on carbon bonding; spectra were collected from zero loss up to 1000 eV energy loss. Micro-Raman spectra were obtained using an argon ion laser operating at 483-514 nm. A Nanoindenter II® system (MTS Instruments, Oak Ridge TN, USA) was used to assess film nanohardness and Young's modulus.

Biofilm attachment studies were done using three microorganisms, *Staphylococcus sp* (wild type), *Pseudomonas aeruginosa* (American Type Culture Collection #10145), and *Candida* (wild type) grown in liquid media. Organisms were grown in nutrient broth (8 g Difco #0003-05-02 in 1L water, pH 6.8, sterilized) at 37 ºC for 15 minutes under 100 kPa on a shaker platform. When log phase growth was obtained, three 1 cm^2 DLC-silver, DLC-silver-platinum, and control chips were rinsed with ethyl alcohol, aseptically added to the media, and incubated for 24, 48 and 72 hours. Incubated materials were then rinsed three times in FA buffer (10 g of Difco #223142 in one liter deionized ultrafiltered (0.2 um) water, pH = 7.2), vortexed for one minute, and then rinsed twice in FA buffer. Samples were then heat fixed at 60 ºC for 12 minutes, stained with 4'-6-Diamidino-2-phenylindole dihydrochloride (DAPI) (0.7 micrograms of DAPI (Sigma Chemical Co. #D9542) per ml phosphate buffer, pH 7.5) for five minutes,

and rinsed with FA buffer. Stained microbial cells were examined and photographed using a Zeiss Axioskop2 plus epifluorescent microscope and a Zeiss Laser Scanning Microscope - 510 Meta using the appropriate filter sets.

Results and Discussion

Transmission electron microscopy

Z-contrast scanning transmission electron microscopy provides unique information on nanostructured composite thin films [13]. An image is formed by scanning a 2.2 Å probe across the sample. The Z-contrast signal is collected from a high angle annular detector, and the electron signal scattered through large angles (typically 75 to 150 mrad) is analyzed. Contrast is proportional to the atomic number (Z) squared. For example, the silver: carbon contrast is over 60:1 and the platinum:carbon contrast is 169:1. Dark field Z-contrast images of diamondlike carbon-silver and diamondlike carbon-platinum nanocomposite films are shown in Figures 2 and 3, respectively. The bright regions correspond to the higher atomic number metal regions, and the dark regions correspond to the DLC matrix. The noble metals are dispersed as nearly spherical metal nanoparticles in arrays within the diamondlike carbon matrix. The average size of these nanocrystalline particles varies between 3 and 5 nm.

Electron energy loss spectra between 280 to 310 eV were acquired. The sp^3 fraction was determined from the K edge loss spectra using an empirical technique developed by Cuomo et al. [14]. In this technique, the peak in the region from 285 to 290 eV results from excitation of electrons from the 1s ground state to the vacant π^*

antibonding state. The peak in the region above 290 eV results from excitation to the higher σ* state. The ratio of the integrated areas under these two energy windows is approximately proportional to the relative number of π and σ* orbitals. Using this information, the atomic fraction of sp^2 bonded carbon (x) can be determined using the expression:

$$(I(\pi)/I(\sigma))_s/(I(\pi)/I(\sigma))_r=3x/(4-x) \quad [2]$$

in which I(π) is the intensity in the range from 284 to 289 eV and I(σ) is the integrated intensity in the range from 290 to 305 eV. The subscripts s and r refer to the ratio determined for the DLC specimen and a reference material with 100% sp^2 bonding, respectively. The sp^3 content was determined to be 63% for a diamondlike carbon film on silicon (100). The sp^3 content was determined to be 47% for a diamondlike carbon-silver nanocomposite film on Si (100) (Figure 4). This data suggests that a moderate reduction in sp^3 content occurs in the metal alloyed films.

Raman spectroscopy

Adhesion of diamondlike carbon thin films is dependent on several factors, including film stress, film/substrate chemical bonding, and substrate topology [15-17]. Large internal compressive stresses as high as 10 GPa have been observed in diamondlike carbon thin films, regardless of the deposition process used. These stresses limit maximum film DLC thickness to 0.1–0.2 micrometers, and prevent widespread medical use. Lifshitz et al. have attributed these stresses to “subplantation” (low energy

subsurface implantation) of carbon ions during diamondlike carbon film growth [18-19]. They suggest that carbon ions with energies between 10-1000 eV undergo shallow implantation to depths of 1-10 nm of during film growth. Carbon species are trapped in subsurface sites due to restricted mobility. This process leads to the development of very large internal compressive stresses.

The Raman spectra of diamondlike carbon thin films contain characteristic peaks that reflect carbon bonding and internal stress. All of the spectra show the following: (1) a broad hump centered in the 1510-1557 cm^{-1} region, which is known as the G- band, and (2) a small shoulder at 1350 cm^{-1}, which is known as the D- band. The G-band is the optically allowed E_{2g} zone center mode of crystalline graphite, and is typically observed in diamondlike carbon films. The D-band is the A_{1g} mode of graphite.

High quality diamondlike carbon films demonstrate the following: (1) a relatively symmetrical G-band, and (2) a lesser D-band, suggesting an absence or a low amount of graphite clusters. The presence of metal atoms leads to greater asymmetry in the G-peak and a slight increase in the height of the D-peak (Figure 5). These features may be produced by a decrease in sp^3 content, an increase in graphitic cluster size within the film, and/or a decrease in compressive stress within the film [20, 21]. The silver and platinum nanoparticles have significantly smaller elastic moduli than the diamondlike carbon matrix; the elastic moduli of silver and platinum are 83 GPa and 168 GPa, respectively. These nanoparticles may be expected to absorb stresses from the diamondlike carbon matrix.

Nanoindentation

During nanoindentation, the modulus of the coated sample approached that of the uncoated sample at roughly 500 nm (~2/3 of the film thickness). Substrate effects were observed at indentation depths of 100 nm. The nanohardness and Young's modulus values for the diamondlike carbon-silver nanocomposite film were determined to be 36.68 +/-6.72 GPa and 332.6+/-38.69 GPa, respectively (Figure 6). These values are similar to those observed in layered WC/DLC and TiC/DLC composites prepared using electron cyclotron resonance chemical vapor deposition or magnetron sputtering techniques (~27 GPa), and are significantly greater than those observed in a-C:H-copper coatings prepared using plasma-enhanced chemical vacuum deposition (PECVD) or hybrid microwave plasma-assisted chemical vapor deposition/sputtering techniques (~10 GPa) [22-26].

Biofilm Attachment Studies

The introduction of implantable medical devices into the body has been shown to greatly increase the risk of infection. Infections involving artificial organs, synthetic vessels, joint replacements, or internal fixation devices usually require reoperation. Some infections are more serious than others; infected cardiac, abdominal, and extremity vascular prostheses result in amputation or death [27-28].

Bacteria form a glycocalyx, an adherent coating that forms on all foreign materials placed within the body [29-31]. This 5-50 μm thick glycoprotein-based coating protects bacteria through a diffusion limitation process, and serves to decrease their antibiotic sensitivity by 10 to 100 times. In addition, the constituents of many alloys and polymers can inhibit both macrophage chemotaxis and phagocytosis. Finally, tissue

damage caused by surgery and foreign body implantation further increases the susceptibility to infection.

The sustained delivery of silver ions into the local implant micro-environment simultaneously exceeds usual systemic concentrations by several orders of magnitude and avoids systemic side effects [32-34]. Silver nanoparticles have been shown to possess an unsurpassed antimicrobial spectrum, with efficacy against 150 different pathogens. Silver ions bind strongly to electron donor groups on sulfur-, oxygen- or nitrogen-containing enzymes. These ions displace other cations (e.g., Ca^{2+}) important for enzyme function. In addition, nanocrystalline silver also provides broad-spectrum fungicidal action. Very low silver ion concentrations required for microbicidal activity (in the range 10^{-9} mol/l). Films containing both silver and platinum may demonstrate enhanced antimicrobial activity due to formation of a galvanic couple that accelerates silver ion release [35].

The results of the biofilm attachment study showed a significant difference in the amount of microbial colonization per unit area between uncoated silicon (100) substrates and DLC-silver and DLC-silver-platinum nanocomposite films. Microbial colonization varied with organism type, incubation period, and composite film type. The gram negative bacteria *Pseudomonas aeruginosa* produced well developed biofilms after 48 hours that were difficult to quantify. The eukaryote, *Candida* wild type, also produced sporadic biofilms at all incubation periods that were difficult to quantify. On the other hand, the gram positive *Staphylococcus sp* also produced a quantifiable biofilm after 24, 48, and 72 hours. Using rich media and long incubation times, impacted biofilm formation on the DLC-metal composite films and control silicon wafers was observed

(Figure 7). The DLC-silver-platinum nanocomposite film demonstrated a one order magnitude lower surface microbial density in gram positive bacteria concentration than the uncoated silicon substrate. Samples showed a difference of between 100 percent to half an order of magnitude lower colonization rates on the DLC-metal nanocomposite films than on the uncoated silicon substrates.

Conclusions

Diamondlike carbon-silver and diamondlike carbon-silver-platinum nanocomposite films were prepared using a novel multicomponent target pulsed laser deposition process. Silver and platinum do not chemically bond with carbon; instead, these metals form nanoparticle arrays within the diamondlike carbon matrix. This self-assembled morphology can be attributed to the high surface energy of noble metals relative to carbon. Ostwald ripening is prevented, and the resulting metal nanoparticles possess uniform size. Raman spectroscopy data suggest that DLC-metal composite films contain lower amounts of internal compressive stress than unalloyed diamondlike carbon films. Silver and platinum exhibit significantly smaller elastic moduli than diamondlike carbon, and may absorb compressive stress from the diamondlike carbon matrix. Nanoindentation testing of the DLC-metal nanocomposite films demonstrates that these films possess hardness and Young's modulus values as high as 37 GPa and 333 GPa, respectively. Finally, diamondlike carbon-silver-platinum nanocomposites exhibit antimicrobial efficacy against *Staphylococcus* bacteria. It is believed that platinum, which is more noble than silver, forms a galvanic couple inside the *in vitro* biofilm testing environment. Silver release (and, by extension, antimicrobial function) is increased in the

diamondlike carbon-silver-platinum nanocomposite films. Diamondlike carbon-biofunctional metal nanocomposite films have a variety of potential medical and antimicrobial applications, including use in orthopaedic, ophthalmic, neurologic, and cardiovascular devices.

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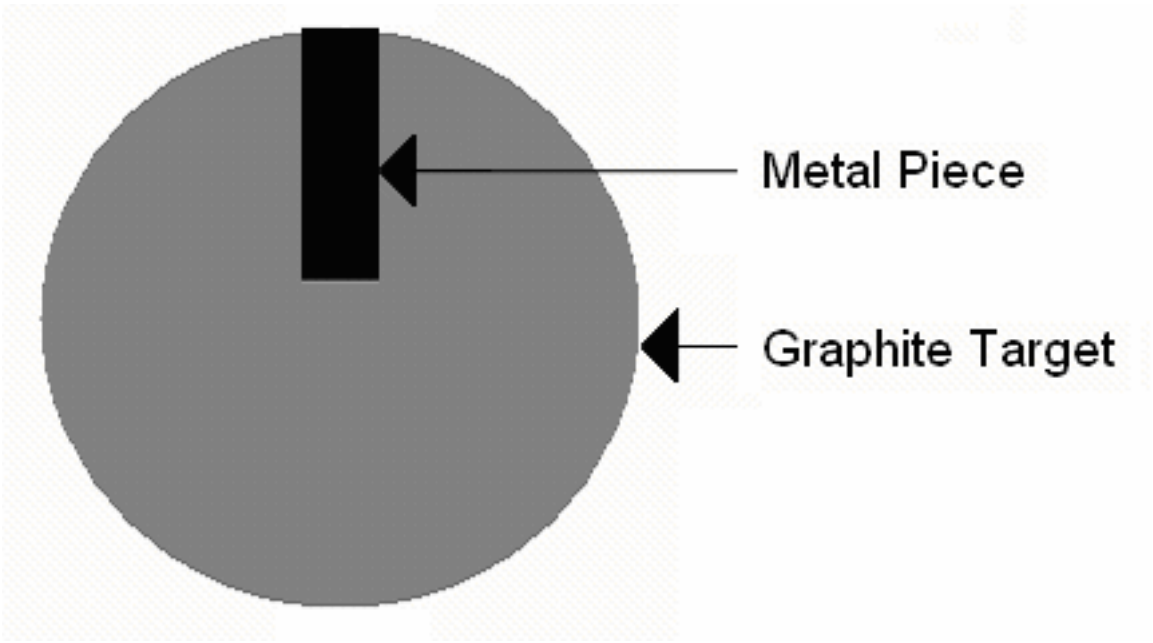

Figure 1. Schematic of target configuration used in this study.

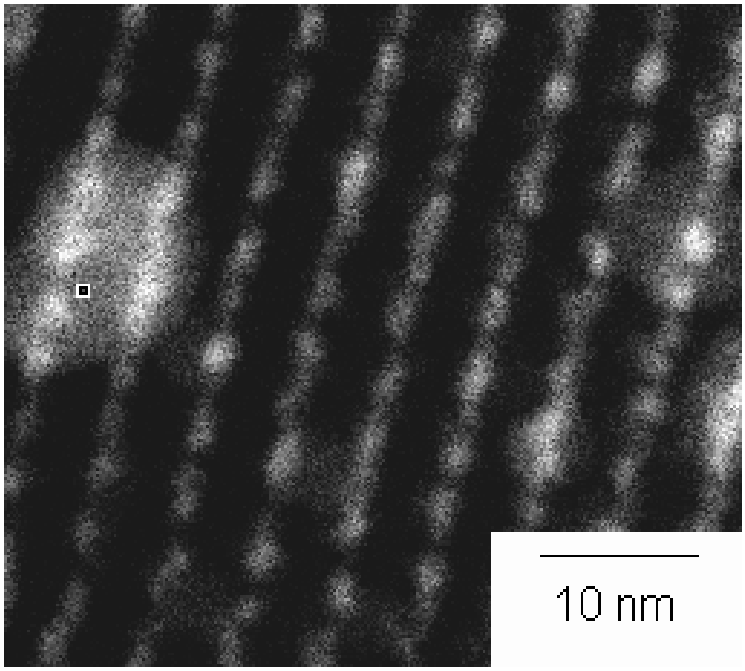

Figure 2. Dark field Z-contrast image of diamondlike carbon-silver nanocomposite film.

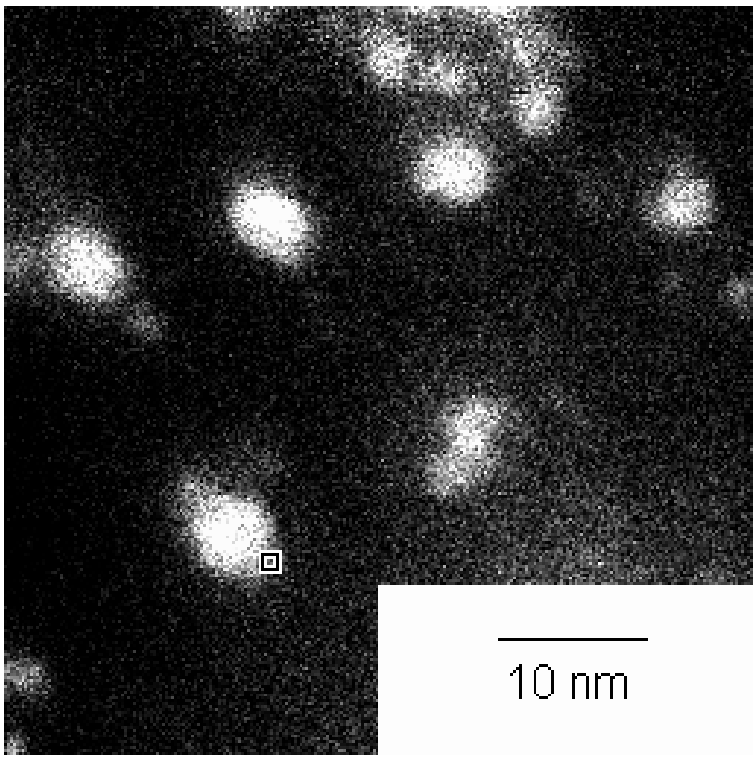

Figure 3. Bright field Z-contrast image of diamondlike carbon-platinum nanocomposite film.

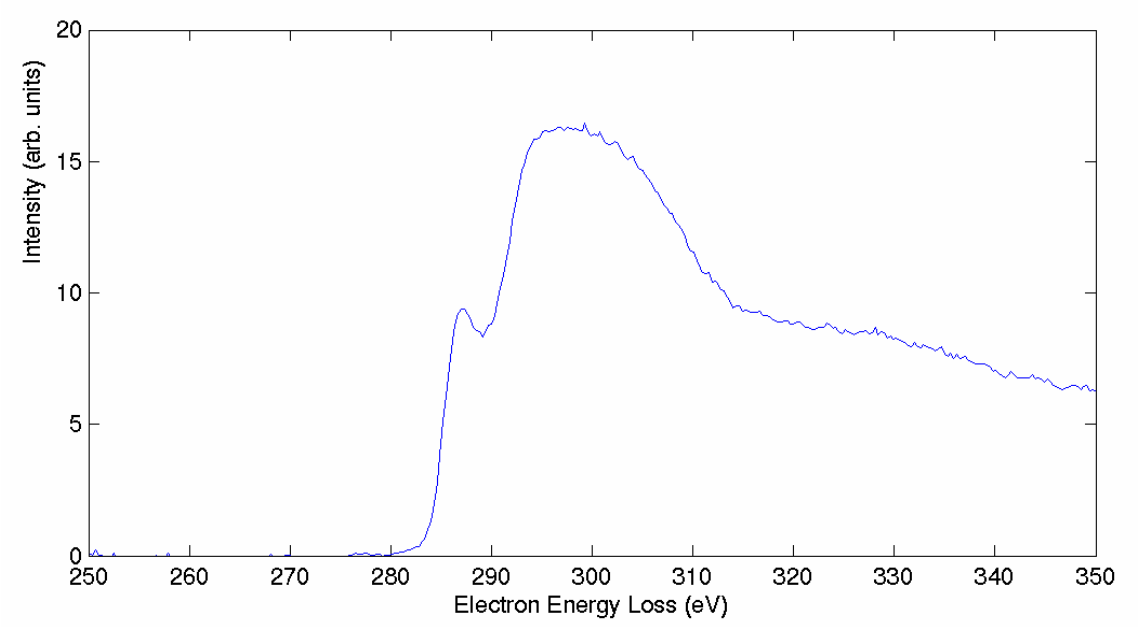

Figure 4. Electron energy loss near the carbon-K edge of diamondlike carbon-silver nanocomposite film.

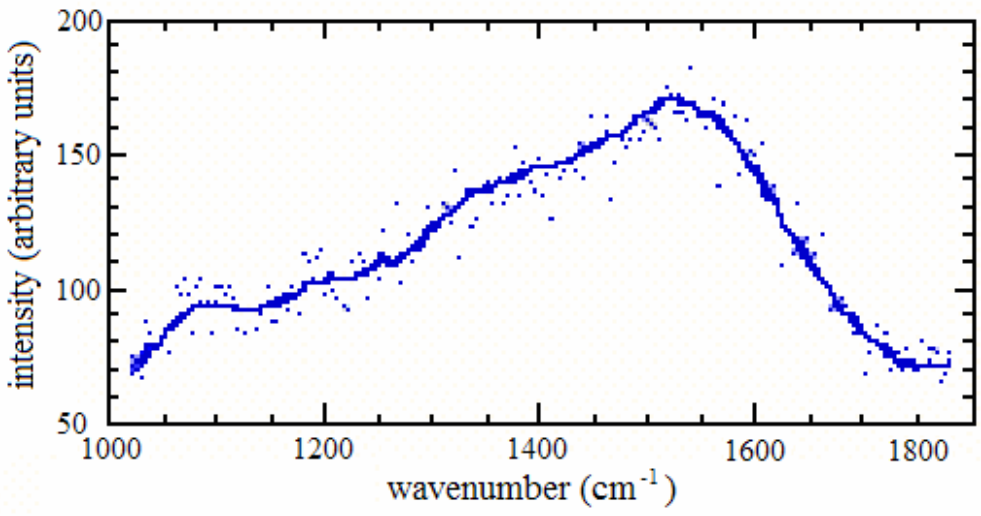

Figure 5. Visible Raman spectrum of diamondlike carbon-silver nanocomposite film.

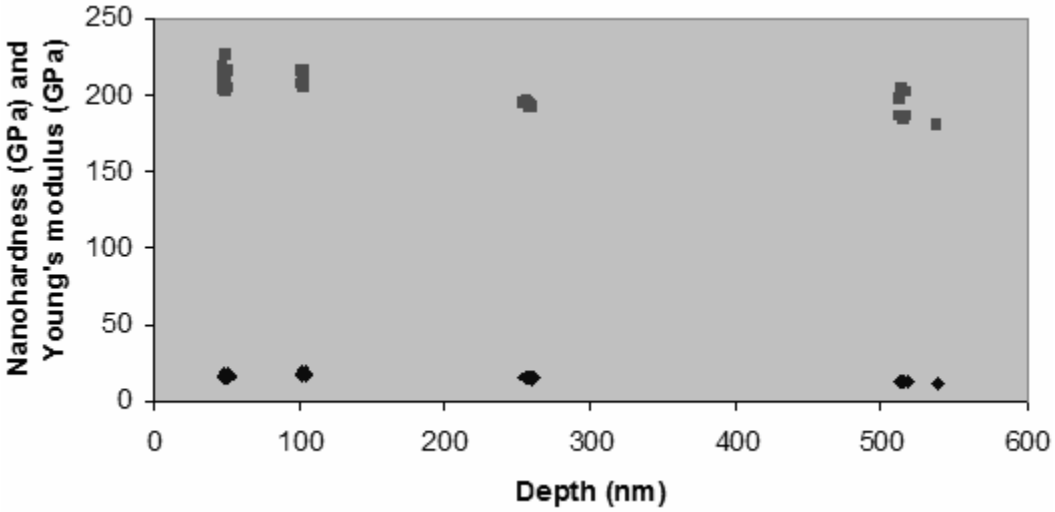

Figure 6. Nanohardness (◆) and Young's modulus (■) values for the diamondlike carbon-silver nanocomposite film. The nanohardness and Young's modulus values for the diamondlike carbon-silver nanocomposite film were determined to be ~36.68 +/-6.72 GPa and ~332.6+/-38.69 GPa, respectively.

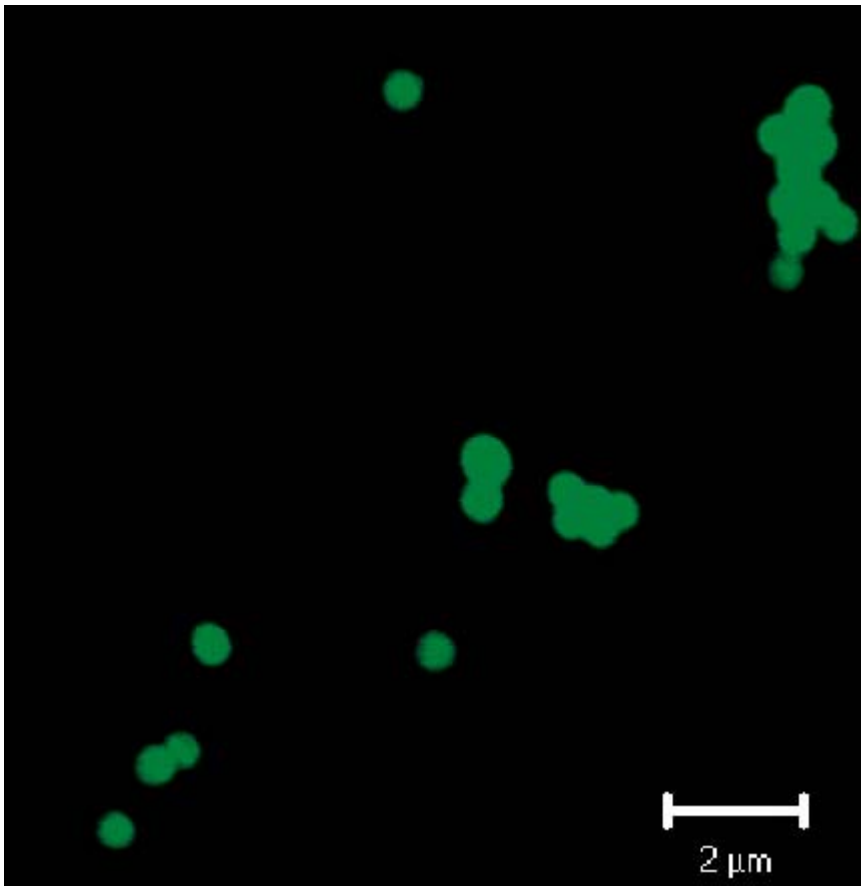

Figure 7. LSM meta system image of diamondlike carbon-silver nanocomposite film inoculated with *Staphlococcus sp.* The DLC-silver-platinum composite film demonstrated a one order magnitude lower surface microbial concentration than the uncoated silicon substrate in *Staphylococcus sp* testing.